Towards practical kesterite photovoltaics: ab initio thermodynamics

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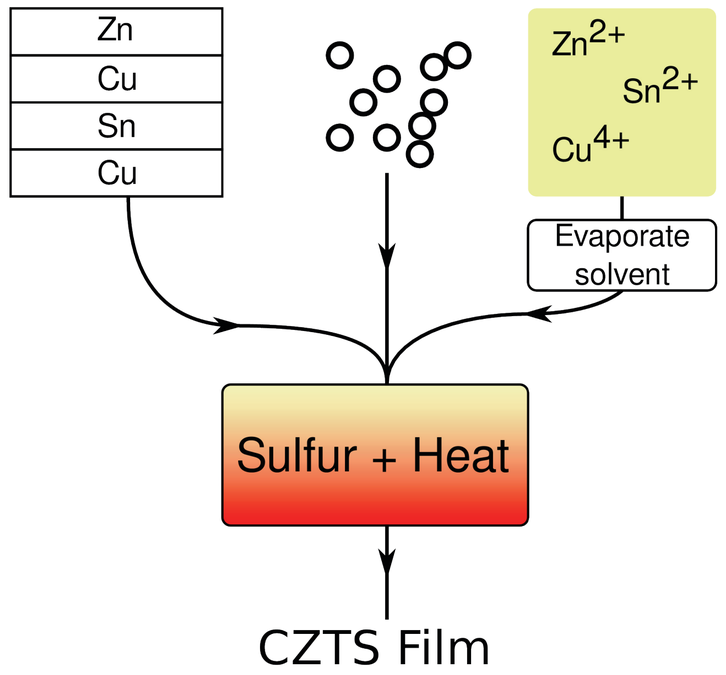
Global photovoltaic (PV) electricity generation is currently of the order 7GW, while global energy consumption (including liquid fuels) is of the order 15TW. In order to make a significant contribution to the energy mixture, PV generation must be hugely expanded. Abundant thin-film absorbers such as Cu_2ZnSnS_4 (CZTS) offer one way forward.

A number of synthesis routes have been identified, but whether the precursors are binary compounds, salts in solution, metal alloys or pre-formed CZTS nanoparticles, film formation typically takes place in a high-temperature annealing process with sulfur vapour. This critical step involves complex phase equilibria and is suited to a thermodynamic study.



Copper zinc tin sulfide films are formed from metals, nanoparticles or salts via an annealing process with sulfur.

Ab initio thermodynamics

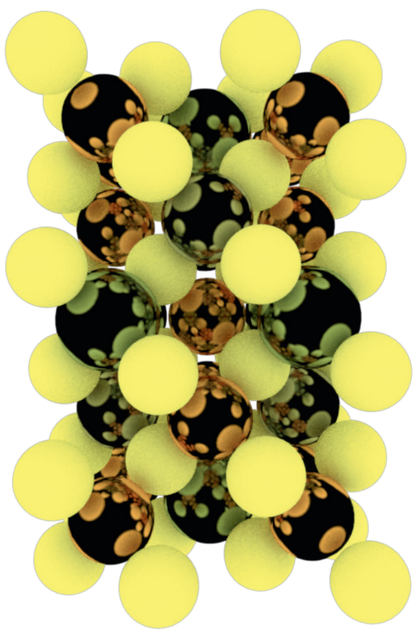
The structures and energies of moderately complex crystalline materials (~100 atoms in a unit cell) may be studied with some confidence using density functional theory (DFT). These methods employ the variational principle to identify the ground state; however, this is not representative of typical usage conditions, and lies even further from industrial reaction conditions. Temperature and pressure effects can be introduced by calculating key bulk properties including the heat capacity and vibrational entropy. By using this data to estimate the chemical potential (μ) for each compound of interest, the Gibbs free energy (ΔG) may be calculated for arbitrary reactions and conditions:

$$\Delta G = \sum_i \mu_i$$

$$\mu = E_{\mathrm{DFT}} + E_{\text{zero-point}} + \int_0^T C_p \mathrm{d}T + PV - TS$$

In the solid state, full phonon spectra may be computed from a series of structures with small displacements to form a set of approximate harmonic normal modes. By filling these modes according to the Boltzmann distribution, free energies can be calculated. Industrial gases are largely well-described in the literature; the challenge lies in bringing the data together to form a consistent model of gas-vapour equilibrium.

Cu_2ZnSnS_4 (CZTS)



Copper zinc tin sulfide (particularly the structure known as kesterite) is a promising next-generation PV absorber material. It is isoelectronic to the currently-popular copper indium gallium selenide (CIGS) thin-film absorber, but all the components are relatively abundant. The most scarce is tin, with reserves of the order 5Gt and annual production of the order 250kt.

Computational details

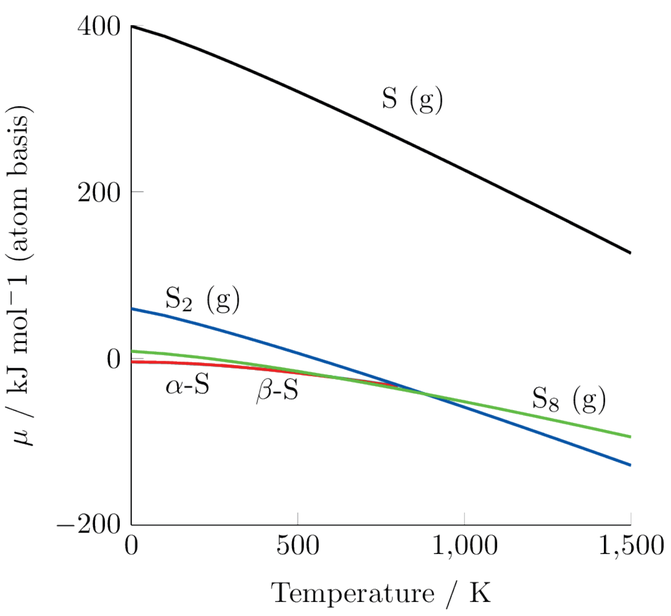
The University of Bath's 800-core Aquila cluster is used for structure optimisation and testing: demanding phonon calculations are carried out on national-scale Cray and Bluegene/Q facilities.

Calculations are primarily carried out using the FHI-aims quantum chemistry code with the PBEsol functional for exchange and correlation.[1] This offers a balance of efficiency and accuracy, while being readily scalable across thousands of computing cores.

Phonon calculations are set up and processed with the "Phonopy" package[2], and thermodynamic modelling is executed with Scientific Python and Matlab.

The sulfur equilibrium

Solid sulfur is an attractive industrial reagent as it is cheap, abundant and relatively safe. However, it is less reactive than some alternatives including H_2S, and forms a complex phase equilibrium. A set of calculated free energies is presented here (drawn from standard data tables[3]) showing the solid crystal (α and β) phases, as well as the major gas phases. In fact a range of cyclic compounds S_2-S_8 exist in equilibrium at the elevated temperatures and low pressures which are preferred for deposition processes.



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[1] Blum, V. et al., Comput. Phys. Commun. 2009, **180**, 2175-2196

[2] Togo, A. et al., Phys. Rev. B. 2008, **78**. 134106

[3] Chase, M. W., J. Phys. Chem. Ref. Data 1998, **Monograph 9**

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